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SYNTHESIS OF ULTRAHIGH MOLECULAR-WEIGHT POLY(ETHYLENE TEREPHTHALATE)

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SUMMARY

This study was conducted to synthesize poly(ethylene terephthalate) or PET of number-average molecular weight of the order of 120 000.

The number-average molecular weight of PET obtained by the ordinary melt polymerization method does not normally exceed 30 000. PET of number-average molecular weight of the order of 120 000 was prepared with a gas chromatograph apparatus through solid-state polymerization technology. PET particles were packed in the column, heated to a temperature somewhat below the melting temperature, and flushed with a carrier gas until the desired molecular weight was reached. Parameters studied were the catalyst, the particle size, the molecular weight of the starting material, the reaction temperature and time, and the flow rate and nature of the carrier gas.

The results showed that ester interchange catalysts such as tetraisopropyl titanate, zinc acetate - antimony trioxide, and cobaltous acetate are capable of increasing the molecular weight of PET. Small particle size and high molecular weight of the starting material are essential for obtaining products of ultrahigh molecular weight. The polymerization of PET in the solid state starts around 175° C (448° K); the molecular weight of the final product increased with increasing temperature for the period of time studied. The preferable polymerization temperature is between 200° and 250° C (473° and 523° K). The optimum reaction time depends on other polymerization variables, including the column size of the gas chromatograph. Molecular weights are also increased by increasing the carrier gas flow rate to a certain practicable value, which varies with other polymerization conditions. Carrier gases used included nitrogen, carbon dioxide, and helium. Their effectiveness in increasing the molecular weights of PET was $N_2 < CO_2 < He$.

INTRODUCTION

Poly(ethylene terephthalate), hereinafter called PET, possesses physical and mechanical properties that are of considerable interest for special aerospace applications at cryogenic temperatures (refs. 1 to 3). The relation between these properties and molecular weight has not been studied. Mark (ref. 4) states that for all polymers certain mechanical properties depend on the average degree of polymerization or average molecular weight and approach a limiting value of strength at degrees of polymerization above 600. Studying the effect of molecular weight on the cryogenic properties of PET required the synthesis of PET with a number-average molecular weight of the order of 120 000 (degree of polymerization $\simeq$ 600). The research on the method of synthesizing ultrahigh-molecular-weight material is presented herein.

PET is ordinarily prepared by reacting dimethyl terephthalate and ethylene glycol in the melted state and distilling methanol and the excess of ethylene glycol in two stages (refs. 5 to 7). However, the number-average molecular weight of PET obtained by this method does not normally exceed 30 000 (ref. 8), primarily because of some side ester interchange reactions involved (refs. 9 and 10). The method of solid-state polymerization was therefore examined as a means of increasing the molecular weight of the material produced by the melt method. In the solid-state method, ethylene glycol can be removed either by employing a high-vacuum technique or by flushing with an inert carrier gas. Gas chromatograph apparatus was discovered to be unusually well suited for performing the desorption of ethylene glycol from PET molecules. Thus, the gas chromatograph apparatus was investigated as a tool for performing the solid-state polymerization. The column of the chromatograph was packed with PET particles instead of the normal absorbent materials.

This report contains a description of the use of a gas chromatograph to perform the solid-state polymerization process and presents the results of attempts to produce ultrahigh-molecular-weight PET. Parameters studied were the catalyst, the particle size, the molecular weight of the starting material, the reaction temperature and time, and the nature and flow rate of the carrier gas.

REACTION MECHANISMS INVOLVED IN POLYMERIZING PET

In the melted state, PET molecules bearing terminal hydroxyl groups are capable of carrying out interchange reactions between the hydroxyl groups and the ester linkages (ref. 9). Another type of interchange between two ester linkages, namely esterolysis, is also possible (ref. 10). These two types of interchange reactions, hydroxyl-ester and ester-ester, may take place either intramolecularly (refs. 10 and 11) or intermo-

lecularly. In addition, the interchange products, in most cases, depend on the position of the reacting ester linkages along the polymer chain. Free ethylene glycol cannot be formed if the reacting ester linkage is in an in-chain position. It can be split off from PET molecules only if a terminal ester linkage is involved. (Here terminal ester linkages refer to those nearest the ends of the polymer chains.) In certain cases of intramolecular reactions, the products formed from the in-chain ester linkages on the same side of the repeating phenylene units as the attacking hydroxyl groups may be different from those on the opposite side. This case may also occur if the attacking group is another ester linkage.

In table I, the possible interchange reactions and their respective products are listed. Reaction I is the only reaction which increases the number-average molecular weight of the product. All other reactions result either in no change or in a decrease in the number-average molecular weight. The decrease in number-average molecular weight results from the formation of cyclic compounds which are, in turn, the consequence of certain intramolecular ester interchange reactions. In the melt polymerization of PET, intramolecular reaction has much less chance to take place than intermolecular reaction (ref. 8). As the polymer chain grows longer, the number of terminal ester linkages becomes less. In other words, at the final stage of melt polymerization, reactions II and VI become predominant. In either of these two ester interchange reactions, there is no net change in the number of interunit linkages before and after the reaction and, therefore, no increase in the number-average molecular weight of the product. Hence, the number-average molecular weight of PET prepared by the melt method normally does not exceed 30 000.

If a polymerization condition could be found such that only the terminal ester linkages, but not the in-chain ones, are activated, intermolecular reactions II and VI would be nearly eliminated. Thus, reaction I, as previously stated, would remain as the only interchange reaction capable of increasing the molecular weight. This condition can be fulfilled if further polymerization of PET is carried out in the solid state. In the solid-state polymerization, the reaction temperature is kept below the melt temperature of PET, but still high enough to activate the terminal ester linkages, so that interchange reactions between the hydroxyl groups of one PET molecule and the adjacent terminal ester linkages of another molecule can still take place. In this type of ester interchange reaction, ethylene glycol is split off, and the number-average molecular weight is increased.

Reaction	Reacting groups	Molecular reaction	Position of ester linkage	Products	Change of number-average molecular weight, $\overline{M}_n$
I	$-OH,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Inter	Terminal	Linear PET; ethylene glycol	Increase
II	$-OH,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Inter	In-chain	Linear PET	None
III	$-OH,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	In-chain, on same side of repeating phenylene units as OH group	Linear PET	None
IV	$-OH,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	In-chain, on opposite side of repeating phenylene units as OH group	Linear PET; cyclic PET	Decrease
V	$-OH,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	Terminal	Cyclic PET; ethylene glycol	Not significant
VI	$-\overset{\displaystyle O}{\overset{\|}{C}}-O,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Inter	Both terminal; both in-chain; terminal and in-chain	Linear PET	None
VII	$-\overset{\displaystyle O}{\overset{\|}{C}}-O,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	Both in-chain, on same side of repeating phenylene units	Linear PET; cyclic PET	Decrease
VIII	$-\overset{\displaystyle O}{\overset{\|}{C}}-O,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	Both in-chain, on opposite side of repeating phenylene units	Linear PET;	None
IX	$-\overset{\displaystyle O}{\overset{\|}{C}}-O,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	Terminal and in-chain, on same side of repeating phenylene units	Linear PET; cyclic PET	Decrease
X	$-\overset{\displaystyle O}{\overset{\|}{C}}-O,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	Terminal and in-chain, on opposite side of repeating phenylene units	Linear PET	None
XI	$-\overset{\displaystyle O}{\overset{\|}{C}}-O,\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-$	Intra	Both terminal	Linear PET	None

EXPERIMENTAL PROCEDURES

Materials

Reagent-grade ethylene glycol was purified by passing it through a column of 60-mesh refrigeration-grade silica gel at room temperature or by distilling it under reduced pressure below 100° C (373° K) with a spinning band column. Dimethyl terephthalate was purified by crystallization from ethyl alcohol and was sublimed at 0.1 millimeter of mercury (0.133×10^2 N/m^2); melting point, 141° to 142° C (414° to 415° K). Practical-grade tetraisopropyl orthotitanate and reagent grade of zinc acetate dihydrate, antimony trioxide, cobaltous acetate tetrahydrate, methylene chloride, and trifluoroacetic acid were used as received. PET samples and carrier gases are listed in tables II and III.

Melt Polymerization of PET

Purified dimethyl terephthalate (4 moles) and ethylene glycol (5 to 10 moles) were charged with catalyst (0.01 to 0.05 percent based on dimethyl terephthalate) into a 2-liter three-neck flask. The melt polymerization procedure is similar to that described in references 5 to 7 and will not be discussed further in this report.

TABLE II. - PET SAMPLES

Form	Catalyst	Melting point		Number-average molecular weight, $\overline{M}_n$	Source
		^{O}C	^{O}K		
Flake	Unknown	254 to 256	527 to 529	15 300	DuPont
Chip	Unknown	256 to 258	529 to 531	16 500	Celanese Plastic
Lump	Ti(OCH(CH$_3$)$_2$)4	256 to 258	529 to 531	2 400	NASA Lewis
Lump	Zn(OAc)$_2$-Sb$_2$O$_3$	254 to 256	527 to 529	8 400	NASA Lewis
Lump	Co(OAc)$_2$	248 to 250	521 to 523	20 000	NASA Lewis

TABLE III. - CARRIER GAS

Carrier gas	Purity, mole percent	Oxygen content, ppm	Moisture content, ppm
N$_2$	99.9	7 to 8	2
CO$_2$	99.5	[a]146	[a]127
He	>99.99	<1	2

[a]Analyzed at Lewis.

Solid-State Polymerization of PET

The PET samples were ground with a Wiley mill and separated by conventional sieves into ranges of 4 to 6, 18 to 20, 60 to 80, and 80 to 200 mesh (NBS series). The ground particles were packed into the gas chromatograph column with gentle tapping. The column was 8 feet (2.4 m) long and 3/4 inch (1.9 cm) in outside diameter and held approximately 300 grams of sample. The melt temperature of each sample was checked with a hot-stage polarized-light microscope before starting polymerization.

The general procedure of solid-state polymerization with a preparative gas chromatograph (ref. 12) is relatively simple. The column packed with PET sample was installed in the chromatograph oven. After the flow of carrier gas was adjusted to the desired rate, the oven was heated and maintained at the reaction temperature for a specified time. A detector and a collection trap may be used but are not necessary. The product was allowed to cool with a minimal flow of the carrier gas. It was then stored in a gas-tight container to avoid moisture absorption.

Number-Average Molecular-Weight Determination

The intrinsic viscosity η measurements of PET were carried out in a solvent mixture of trifluoroacetic acid and methylene chloride (1 to 1 by volume) with a Ubbelohde viscometer at 25° C (298° K). (The solvent mixture was recommended in a private communication with Dr. C. J. Heffelfinger of Dupont.) Number-average molecular weights $\overline{M}_n$ were calculated from Mark-Houwink equation

$$\eta = K\overline{M}_n^a$$

where K and a were determined to be 9.2×10^{-4} and 0.70, respectively, by employing a set of PET samples of known number-average molecular weights from 14 000 to 28 000.

RESULTS AND DISCUSSION

Effect of Catalyst

Coover, Joyner, and Shearer (ref. 13) indicate that an organotitanium compound has to be used as the catalyst in a solid-phase polymerization process for preparing linear superpolyesters. The results summarized in table IV, however, show that other com-

TABLE IV. – EFFECT OF CATALYST ON SOLID-STATE POLYMERIZATION OF

PET USING GAS CHROMATOGRAPH APPARATUS

[Reaction temperature, 250° C (523° K); test period, 24 hr; particle diameter,
0.18 to 0.25 mm; chromatograph column size, 8 feet (2.4 m) by 3/4-in. –
(1.9-cm-) o.d.; nitrogen gas flow rate, 350 milliliter/min.]

PET sample	Catalyst	Number-average molecular weight, $\overline{M}_n$		Source
		Initial	Final	
1	Unknown	15 300	80 000	DuPont
2	Unknown	16 500	104 000	Celanese Plastic
3	Tetraisopropyl titanate	2 400	18 000	NASA Lewis
4	Zinc acetate and antimony trioxide	8 400	65 000	NASA Lewis
[a]5	Cobaltous acetate	20 000	[b]>120 000	NASA Lewis

[a]Reaction temperature, 230° C (503° K); nitrogen for 24 hours and helium for
12 hours.
[b]Not completely soluble in solvent mixture of trifluoroacetic acid and methylene
chloride (1 to 1 by volume).

monly used ester interchange catalysts such as zinc acetate – antimony trioxide and co-
baltous acetate are also capable of increasing the molecular weights of PET. These re-
sults suggest that polymerization of PET in the solid state is essentially the elimination
or minimization of undesired interchange reactions involving the in-chain ester link-
ages. Any type of catalyst which affects the polymerization of PET in the melted state
should be also effective in the solid state as long as the reaction temperature is high
enough to activate the terminal hydroxyl groups and those ester linkages nearest the ends
of the chains. It is well known that the nature and amount of catalyst used in polyester-
ification can affect the molecular weight of the product. The knowledge obtained from a
great deal of research on catalysts (refs. 14 and 15) for the melt polymerization of PET
may be applied to the solid-state polymerization as well.

Effect of Initial Molecular Weight

The results summarized in table IV show that the final molecular weight of the prod-
uct is more dependent on the molecular weight of the starting material than on the na-
ture of the catalyst. Apparently, in solid-state polymerization the chances for the re-
acting groups to come together are limited, and the removal of ethylene glycol is also
restrained because of solid-phase diffusion problems. Within the same interval of re-

action time, the higher the molecular weights of the starting materials, the higher the molecular weights of the products that should be expected.

Effect of Reaction Temperature

Figure 1(a) shows the relation between the reaction temperature and the molecular weight of the final product. The starting material had a number-average molecular weight of 16 500. There is no appreciable degree of further polymerization below 150° C (423° K) for the period of time studied. The reaction starts around 175° C (448° K), and the molecular weight of the product increases with temperature to 250° C (523° K), which is close to the melting temperature of the PET sample (254° to 256° C or 527° to 529° K). However, in solid-state polymerization, PET of ultrahigh molecular weight does not have to be obtained at the highest allowable reaction temperature. Theoretically, the sample would eventually reach the same molecular weight as long as the reaction temperature is kept above 175° C (448° K).
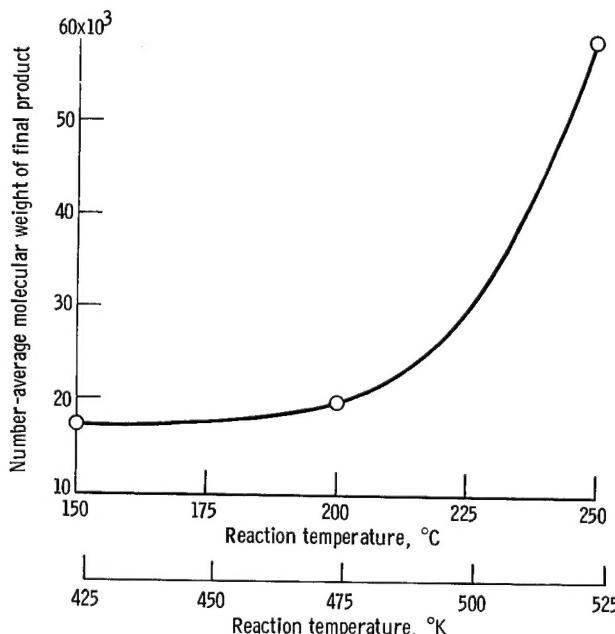

(a) Effect of reaction temperature. Test period, 7 hours; particle diameter, 0.18 to 0.25 millimeter; nitrogen gas flow rate, 350 milliliters per minute.

Figure 1. - Effects of reaction temperature, reaction time, particle size, and nitrogen gas flow rate on solid-state polymerization of PET using gas chromatograph apparatus. Initial number-average molecular weight, 16 500; chromatograph column size, 8 feet (2.4 m) by 3/4-inch- (1.9-cm-) outside diameter.

8

Effect of Reaction Time

As shown in figure 1(b), the solid-state polymerization was carried out at 250° C (523° K), and the number-average molecular weights of the final products were plotted against the reaction time. There is an optimum time (about 40 hours in this case) for the process to reach the stage of maximum molecular weight ($\overline{M}_n$, 120 000). Beyond this point the curve slopes downward instead of remaining flat. Since under the condition of solid-state polymerization, cyclic compounds can hardly be formed, the decrease in molecular weight apparently is caused by chain degradations which become predominant as the reaction time gets longer. The most probable degradation is the thermal type
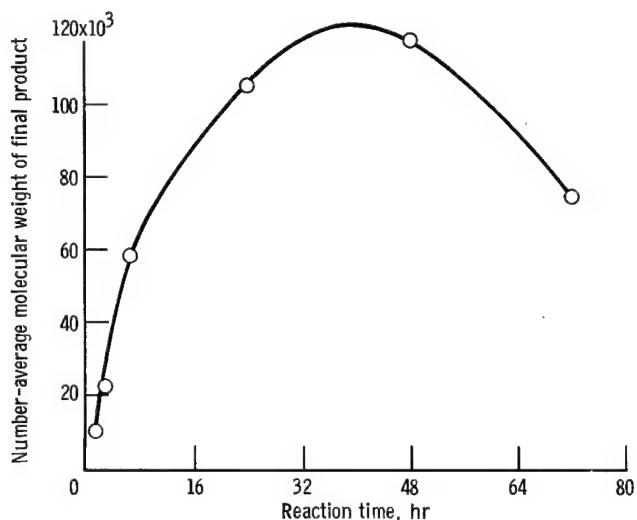
(b) Effect of reaction time. Reaction temperature, 250° C (523° K); particle diameter, 0.18 to 0.25 millimeter; nitrogen gas flow rate, 350 milliliters per minute.

Figure 1. – Continued.

(ref. 8), which may be minimized by adopting a relatively lower reaction temperature. Oxidative and hydrolytic degradations (refs. 16 and 17) due to the small amount of oxygen and moisture content in the carrier gas cannot be ruled out. These side reactions can be eliminated by passing the inert carrier gas through a train of absorption columns containing copper filings heated to above 500° C (773° K) and molecular sieves or silica gel.

Effect of PET Particle Size

Figure 1(c) indicates that increased molecular weight is obtained by decreasing the PET particle size. Since decreasing the particle size not only increases the reaction
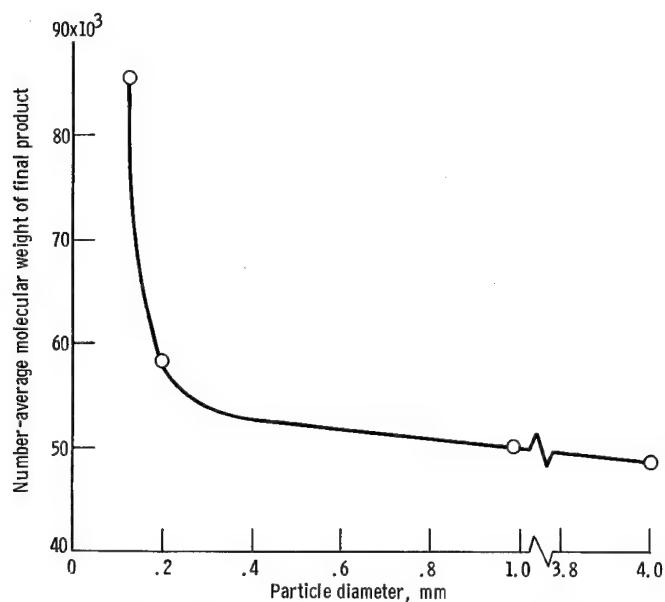
(c) Effect of particle size. Reaction time, 7 hours; reaction temperature, 250° C (523° K); nitrogen gas flow rate, 350 milliliters per minute.
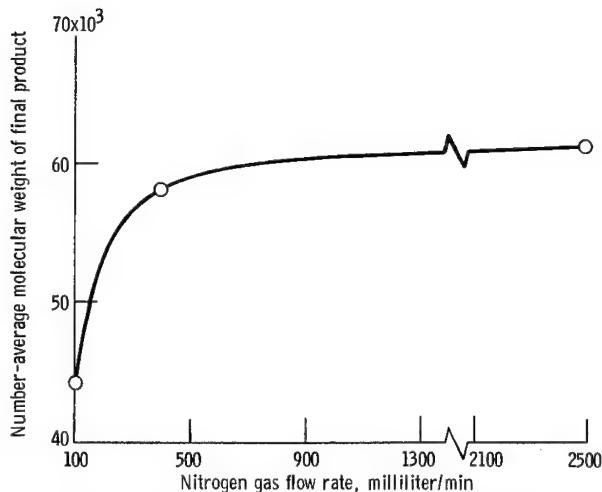
(d) Effect of nitrogen gas flow rate. Test period, 7 hours; reaction temperature, 250° C (523° K); particle diameter, 0.18 to 0.25 millimeter.

Figure 1. - Concluded.

sites of polymerization but also facilitates the removal of ethylene glycol, this result was expected.

Effect of Gas Flow Rate

Figure 1(d) shows the variation of molecular weight with the nitrogen gas flow rate. There is an optimum value of the flow rate above which only a modest increase in molecular weight is obtained. The optimum value in this study is 500 milliliters per minute.

Effect of Carrier Gas

The effect of the carrier gas on the molecular-weight increase is as follows:

Nitrogen 58 000

Carbon dioxide 81 000

Helium 90 000

where the reaction temperature was 250° C (523° K), the test period was 7 hours, the

10

PET particle diameter was 0.18 to 0.25 millimeter, the initial number-average molecular weight was 16 500, the chromatograph column size was 8 feet (2.4 m) by 3/4-inch- (1.9-cm-) outside diameter, and the gas flow rate was 350 milliliters per minute.

The order ($N_2 < CO_2 < He$) of this effect is interesting. If the gases simply functioned as the carrier for ethylene glycol vapor, there should have been no significant difference in the final molecular weights. In other words, their influence on the molecular-weight increase should be nearly equal. If the desorption of the ethylene glycol molecules from PET were affected only by the diffusion of the gas through the solid phase, their effectiveness should be inversely proportional to their molecular sizes and would be in the order of $CO_2 < N_2 < He$. The discrepancy could arise from the intermolecular forces of attraction between ethylene glycol and the gases, which are expected to be $He \leq N_2 < CO_2$. Because of these two main factors, diffusion and intermolecular forces, the experimental findings, $N_2 < CO_2 < He$, appear reasonable.

Extensions of Solid-State Polymerization Using Gas Chromatograph Apparatus

Following the program discussed in this report, additional PET was polymerized on a larger scale by using the 4-inch- (0.1-m-) outside-diameter columns. As much as 20 pounds per operation (about 10 kg) could be processed in this fashion. A number-average molecular weight of 68 000 was obtained from a 20-pound ($\sim$10-kg) sample of Celanese PET polymerized at 250° C (523° K) for 48 hours with a helium flow rate of 1 liter per minute.

It is possible that with selection of the proper polymerization variables, this larger scale process could be used to synthesize PET with a number-average molecular weight of the order of 120 000.

In addition to its use for the solid-state polymerization of PET, the gas chromatographic process should also be suitable for synthesizing ultrahigh-molecular-weight products of other condensation-type polymers such as other polyesters, polyamides, and polyimides.

CONCLUSION

The results of the investigation of the solid-state polymerization of poly(ethylene terephthalate) or PET performed with a gas chromatograph show that a final product of number-average molecular weight in excess of 120 000 may be obtained from commercial-grade materials by adopting the most favorable combination of the param-

eters studied. Ester interchange catalysts such as tetraisopropyl titanate, zinc acetate - antimony trioxide, and cobaltous acetate are all capable of increasing the molecular weight of PET. Smaller particle size and higher molecular weight of the starting material are essential for achieving the ultrahigh-molecular-weight product. The preferable reaction temperature is between 200° and 250° C (473° and 523° K). The optimum reaction time depends on other polymerization variables, including the column size of the gas chromatograph. Molecular weights are also increased by increasing the gas flow rate to an optimum value, which varies with other polymerization conditions. The inert gas increases molecular weight in the order nitrogen, carbon dioxide, and then helium. The gas chromatographic process of solid-state polymerization can be used to prepare relatively large quantities (as much as 20 lb (~10 kg) per operation) of ultrahigh-molecular-weight PET by using 4-inch- (0.1-m-) outside-diameter columns.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, October 3, 1967,
            129-03-11-01-22.

REFERENCES

1. Mowers, R. E.; Lieb, J. H.; Sherman, S.; Davenport, C. K.; and Reiner, P. J.: Final Report, Program of Testing Nonmetallic Materials at Cryogenic Temperatures. Rep. No. R-3498, Rocketdyne Div., North American Aviation, Dec. 30, 1962.

2. Bell, J. E.; Killian, W. R.; Penner, J. E.; Pope, D. H.; Sutton, H. E.; and Tweed, R. M.: Development of Positive Expulsion Systems for Cryogenic Fluids. Eng. Rep. No. 13511 (AFSSD-TDR-62-14), Beech Aircraft Corp., May 1962.

3. Hanson, Morgan P.; Richards, Hadley T.; and Hickel, Robert O.: Preliminary Investigation of Filament-Wound Glass-Reinforced Plastics and Liners for Cryogenic Pressure Vessels. NASA TN D-2741, 1965.

4. Mark, H. F.: Polymers in Material Science. J. Polymer Sci., Part C, no. 9, 1965, pp. 1-33.

5. Sorenson, Wayne R.; and Campbell, Tod W.: Poly(ethylene terephthalate). Preparative Methods of Polymer Chemistry. Interscience Publishers, 1961, p. 113.

6. Cramer, Francis B.: Poly(ethylene terephthalate). Macromolecular Syntheses. Vol. 1. C. G. Overberger, ed., John Wiley & Sons, Inc., 1963, pp. 17-21.

7. Smith, James G.; Kibler, Charles J.; and Sublett, Bobby J.: Preparation and Properties of Poly(methylene terephthalates). J. Polymer Sci., Part A-1, vol. 4, no. 7, 1966, pp. 1851-1859.

8. Goodman, I.; and Rhys, J. A.: Polyesters. Vol. I. American Elsevier, 1965, ch. 3.

9. Flory, Paul J.: Principles of Polymer Chemistry. Cornell University Press, 1953, ch. 3.

10. Korshak, V. V.; and Vinogradova, S. V.: Polyesters. Pergamon Press, 1964, ch. 6.

11. Hashimoto, Shizunobu; and Sakai, Junichi: Formation of Cyclic Ethylene Terephthalate Oligomers by the Thermal Degradation of Poly(ethylene Terephthalate). Kobunshi Kagaku, vol. 23, no. 254, 1966, pp. 422-425.

12. Anon.: Model 775 Prepmaster Instruction Manual. F and M Scientific, Division of Hewlett Packard Company.

13. Coover, H. W., Jr.; Joyner, F. B.; and Shearer, Jr., N. H.: Solid Phase Process for Linear Superpolyesters. U.S. Patent 3,075,952, 1963.

14. Griehl, W.; and Schnock, Gunther: The Kinetics of Polyester Formation by Transesterification. J. Polymer Sci., vol. 30, 1958, pp. 413-422.

15. Wilfong, R. E.: Linear Polyesters. J. Polymer Sci., vol. 54, 1961, pp. 385-410.

16. Buxbaum, L. H.: Reaction of Molecular Oxygen with Poly(ethylene terephthalate). Polymer preprints, Miami Beach Meeting, American Chemical Society, 1967, p. 552.

17. Marshall, I.; and Todd, A.: The Thermal Degradation of Polyethylene Terephthalate. Trans. Faraday Soc., vol. 49, 1953, pp. 67-78.

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